

APPLICATION UNDER UNITED STATES PATENT LAWS

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Invention: RUBBER MIXTURES

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This is a:

- ☐ Provisional Application
 - ☒ Regular Utility Application
 - ☐ Continuing Application
 - ☐ PCT National Phase Application
 - ☐ Design Application
 - ☐ Reissue Application
 - ☐ Plant Application
 - ☐ Substitute Specification
- Sub. Spec Filed _____
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SPECIFICATION

RUBBER MIXTURES

CROSS-REFERENCE TO RELATED APPLICATION

This application is based on German Application DE 199 15 281.0, filed April 3,
5 1999, which disclosure is incorporated herein by reference.

FIELD OF THE INVENTION

The present invention relates to rubber mixtures, to a process for their
preparation and to the production of moldings using the rubber mixtures.

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BACKGROUND OF THE INVENTION

It is known to use sulfur-containing organosilicon compounds, such as 3-
mercaptopropyltrimethoxysilane, 3-thiocyanatopropyltriethoxysilane or bis(3-
15 {triethoxysilyl}propyl)tetrasulfane, as silane coupling agents or reinforcing
additives in oxide-filled rubber mixtures, inter alia for the production of treads
and other parts of automobile tires (DE 2 141 159, DE 2 212 239,
DE 195 444 69 A1, US 3 978 103, US 4 048 206, EP 784 072 A1).

The additional use of alkylsilanes in rubber mixtures to reduce the mixing
20 viscosity is also known (EP 795 577 A1, EP 864 605 A2).

In the preparation of rubber mixtures with organosilanes and a filler, for
example a precipitated silicic acid, a chemical reaction takes place during the
mixing process, for example in an internal mixer. This chemical reaction is a
25 condensation reaction which is accompanied by the release of a considerable
amount of alcohol. As described in the literature [A. Hunsche, U. Görl, A.
Müller, M. Knaack, T. Göbel, *Kautsch. Gummi, Kunstst.* **50**, 881 (1997)], this
condensation reaction is made up of a primary reaction, in which an ethoxy
group reacts with a silanol group from the silicic acid, and a secondary reaction
30 between two ethoxy groups, which results in crosslinking between the silane
molecules. According to the state of the art, up to three mol of ethanol can be
eliminated per mol of silicon by these reactions when silanes containing three
ethoxy functional groups are used.

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In some cases this eliminated alcohol causes appreciable technical problems in the further processing of the rubber mixtures, such as the porosity of the mixture during extrusion or undesired blistering in the rubber itself.

- 5 Furthermore, it is in the interest of health and the environment to reduce the amount of alcohol released during the reaction.

SUMMARY OF THE INVENTION

- 10 It has now been found that these disadvantages in the state of the art can be greatly mitigated by the use of organosilanes in which the trialkoxysilyl functional group used hitherto is replaced with silyl functional groups containing fewer alkoxy groups.

- 15 Accordingly, the present invention relates to the use of organosilanes of the general structure $R^1R^2R^3Si-R^4-Z$ (I), in which the organosilane contains fewer than 3 ethoxy groups per silicon atom.

- The invention provides rubber mixtures which are characterized in that they
20 contain organosilanes of the general structure



- wherein R^1 , R^2 and R^3 independently of one another are H, (C_1-C_4) alkyl, (C_1-C_4) alkoxy or halogen and the number of alkyl groups is ≥ 1 ;
25

R^4 is a linear or branched (C_1-C_{18}) alkylidene group; and
 $Z = H$, halogen, SCN, SH or $S_x-R^4-SiR^1R^2R^3$, where x is 2 to 10.

- 30 Preferred organosilanes of the type described above are those with dialkylmonoalkoxysilyl functional groups in place of the trialkoxysilyl functional groups conventionally used. Particularly preferred silanes are the bis(3-{dimethylethoxysilyl}polysulfanes) according to the invention.

Rubber mixtures according to the invention may include organosilanepolysulfane and organoalkylsilane compounds. The organosilanepolysulfane may be a silane in which R^1 = ethoxy or methoxy, $R^2 = R^3$ = methyl, R^4 = propylidene or isobutylidene and $Z = S_x-R^4-SiR^1R^2R^3$, where x has a statistical mean value of 2 to 4. In another embodiment, the organoalkylsilane may be a silane in which R^1 = ethoxy or methoxy, $R^2 = R^3$ = methyl and $R^4 = (C_1-C_{18})$ alkylidene.

- 10 The present invention therefore provides rubber mixtures containing rubber, filler, especially including precipitated silicic acid, optionally other rubber auxiliaries, and at least one organosilane which is built up of the structural units described above and which is used in amounts of 0.1 to 15 wt.%, based on the amount of rubber used. The organosilane may include an
- 15 organosilanepolysulfane such as bis(3-{dimethylethoxysilyl}propyl)tetrasulfane or bis(3-{dimethylethoxysilyl}propyl)disulfane, optionally with an alkylsilane.

Because of the smaller number of alkoxy groups in the organosilanes of general structure (I), the disadvantageous release of alcohol is reduced when

20 these organosilanes are used in rubber mixing processes. Compared with the known procedure, e.g. using bis(3-{triethoxysilyl}propyl)tetrasulfane (TESPT) as coupling agent, the maximum possible release of alcohol is reduced by 66%.

- 25 Surprisingly, it has now also been found that the rubber mixtures prepared with the silanes according to the invention, and the vulcanizates prepared therefrom, do not exhibit any disadvantages in respect of their engineering properties compared with the comparative reference material containing a triethoxysilyl functional group, according to the state of the art (See
- 30 Comparative Example 1 and Inventive Example 2).

The organosilanes according to the invention and the fillers are preferably added at stock temperatures of 100° to 200° C, but they can also be added

later at lower temperatures (40° to 100°C), for example, together with other rubber auxiliaries.

5 The organosilanes can be introduced into the mixing process either in pure form or adsorbed on an inert organic or inorganic carrier. Preferred carrier materials are silicic acids, natural or synthetic silicates, aluminum oxide or carbon blacks.

10 The following fillers are suitable for the rubber mixtures according to the invention:

- 15 - Carbon blacks: The carbon blacks to be used here are prepared by the lamp black, furnace black or gas black process and have BET surface areas of 20 to 200 m²/g, e.g. SAF, ISAF, HSAF, HAF, FEF or GPF carbon blacks. The carbon blacks can optionally also contain heteroatoms such as Si.
- 20 - Highly disperse silicic acids, prepared e.g. by the precipitation of silicate solutions or the flame hydrolysis of silicon halides, with specific surface areas of 5 to 1000, preferably 20 to 400 m²/g (BET surface area), and with primary particle sizes of 10 to 400 nm. The silicic acids can optionally also take the form of mixed oxides with other metal oxides such as Al, Mg, Ca, Ba, Zn and titanium oxides.
- 25 - Synthetic silicates, such as aluminium silicate, or alkaline earth metal silicates like magnesium silicate or calcium silicate, with BET surface areas of 20 to 400 m²/g and primary particle diameters of 10 to 400 nm.
- 30 - Natural silicates, such as kaolin and other naturally occurring silicic acids.
- Glass fibers and glass fiber products (mats, strands) or glass microspheres.

It is preferred to use carbon blacks with BET surface areas of 20 to 400 m²/g or highly disperse silicic acids, prepared by the precipitation of silicate solutions,

with BET surface areas of 20 to 400 m²/g in amounts of 5 to 150 parts by weight, based in each case on 100 parts of rubber.

These fillers can be used separately or in a mixture. In one particularly preferred embodiment of the process, the mixtures are prepared using 10 to 150 parts by weight of white fillers, optionally together with 0 to 100 parts by weight of carbon black, and 0.3 to 10 parts by weight of a compound of formula (I), based in each case on 100 parts by weight of rubber.

Apart from natural rubber, synthetic rubbers are also suitable for preparing the rubber mixtures according to the invention. Preferred synthetic rubbers are described for example in W. Hofmann, Kautschuktechnologie (Rubber Technology), Genter Verlag, Stuttgart 1980. They include inter alia:

- polybutadiene (BR)
- polyisoprene (IR)
- styrene/butadiene copolymers with styrene contents of 1 to 60 wt.%, preferably 2 to 50 wt.% (SBR)
- isobutylene/isoprene copolymers (IIR)
- butadiene/acrylonitrile copolymers with acrylonitrile contents of 5 to 60 wt.%, preferably 10 to 50 wt.% (NBR)
- partially hydrogenated or fully hydrogenated NBR (HNBR)
- ethylene/propylene/diene copolymers (EPDM)

and mixtures of these rubbers. Anionically polymerized solution SBRs with a glass transition temperature above -50°C, and mixtures thereof with diene rubbers, are of particular interest for the production of automobile tires.

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A4

Table 1

Substance	Amount [phr]
1st stage	
BUNA VSL 5025-1	96.0
BUNA CB 24	30.0
ULTRASIL VN3	80.0
ZnO	3.0
Stearic acid	2.0
NAFTOLEN ZD	10.0
VULKANOX 4020	1.5
PROTEKTOR G35P	1.0
Silane	acc. to Ex. 1, 2
2nd stage	
Batch stage 1	
3rd stage	
Batch stage 2	
PERKACIT TBZTD	0.2
VULKACIT D	2.0
VULKACIT CZ	1.5
Sulfur	1.5

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The polymer BUNA CB 24 is a cis-1,4-polybutadiene (neodymium type) from Bayer AG with a cis-1,4 content of 97%, a trans-1,4 content of 2%, a 1,2 content of 1% and a Mooney viscosity of between 39 and 49.

The silicic acid ULTRASIL VN3 from Degussa AG has a BET surface area of 175 m²/g. TESP (bis(3-[triethoxysilyl]propyl)disulfane) of Comparative Example 1 is prepared according to patent DE 195 414 04. The silane of Example 2, bis(3-[dimethylethoxysilyl]propyl)disulfane, is prepared according to the state of the art by the hydrosilylation of chlorodimethylsilane with allyl chloride, followed by ethanolysis and sulfurization analogously to the process indicated in patent DE 197 342 95 A1.

The aromatic oil used is NAFTOLEN ZD from Chemetall. VULCANOX 4020 is PPD from Bayer AG and PROTEKTOR G35P is an antiozone wax from HB-Fuller GmbH. VULKACIT D (DPG) and VULKACIT CZ (CBS) are commercial products from Bayer AG. PERKACIT TBZTD is a commercial product from Flexis S.A.

The engineering properties of the rubber are tested by the methods indicated in Table 2.

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